

# Nonlinear Optical Materials

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## INTRODUCTION

There has been a growing interest in fundamental and scientific research in the area of molecule-based nonlinear optical (NLO) materials with large second- and third-order nonlinearities. The research was primarily motivated by applications of optical and electro-optical devices based on these materials in the telecommunications and optical data-processing industries.<sup>[1]</sup> In particular, second-order NLO materials offer many attractions, such as large nonresonant ultrafast response times, low dielectric constants, and intrinsic architectural tailorability.<sup>[2]</sup> The noncentrosymmetric organization of chromophores is an essential requirement for efficient bulk second-order nonlinear optical materials. Thus, the controlled construction of supramolecular assemblies has become a popular method in the design and synthesis of NLO materials. A variety of methods such as electric field poling,<sup>[3–6]</sup> Langmuir–Blodgett assembly,<sup>[7,8]</sup> and crystal engineering<sup>[9–13]</sup> were employed to prepare second-order NLO materials. In the last decade, the layer-by-layer molecular self-assembly approach was tremendously active in the development of new NLO materials.<sup>[14]</sup> In this article, we discuss the concept of optical nonlinearity and the strategies for design and synthesis of nonlinear optical chromophores and supramolecular structures.

## THE CONCEPT OF OPTICAL NONLINEARITY

When the electric field of electromagnetic radiation interacts with a material, it induces a dipole moment in the material. The dipole moment induced per unit volume is called “polarization.” At low electric fields, the macroscopic polarization or polarization of the bulk medium,  $P$ , is linearly related to the field by the proportionality constant,  $\chi^{(1)}$ , known as the linear electric susceptibility. At high fields, typically those associated with lasers, contribution of the nonlinear (second- and

higher-order) terms becomes significant.<sup>[15]</sup> Higher-order susceptibilities  $\chi^{(n)}$  ( $n > 1$ ) are inherently much smaller than  $\chi^{(1)}$ , and progressively become smaller as  $n$  increases. The polarization component along the  $i^{\text{th}}$  axis can, therefore, be generally represented as follows:

$$P_i = \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \quad (1)$$

Because the electric field and the polarization are vectors, the  $n^{\text{th}}$ -order macroscopic electric susceptibility ( $\chi^{(n)}$ ) that relates the components of the polarization to the applied field, is an  $(n + 1)$ -order tensor. The microscopic polarization in molecules is defined by the induced dipole moment  $p_i$ , which depends on the molecular polarizability,  $\alpha$ , and hyperpolarizabilities,  $\beta$ ,  $\gamma$ , etc., as follows:

$$p_i = \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \dots \quad (2)$$

In Eqs. 1 and 2, the indices  $i$ ,  $j$ ,  $k$ , and  $l$  refer to the coordinate system of the bulk material and molecule, respectively. Illustrated in Fig. 1 are the linear and nonlinear polarizations with respect to electric field. The Fourier decomposition of this nonlinear polarization comprising components of zero frequency, the fundamental frequency, the second-harmonic frequency, the third-harmonic frequency, etc., is shown in Fig. 2. The effects up to the second order, which are easily observed experimentally, are called the optical rectification,  $P(0)$ ; linear electro-optic effect  $P(\omega)$ ; second-harmonic generation  $P(2\omega)$ , and third-harmonic generation  $P(3\omega)$ .

## Second-Harmonic Generation (SHG)

The phenomenon of frequency doubling or second-harmonic generation can be visualized as follows. If the applied electric field is of frequency  $\omega$ , it can be represented as  $\sin \omega t$ , and the quadratic terms are seen to have a  $2\omega$  dependence.

$$E \propto \sin \omega t$$

$$E^2 \propto \sin^2 \omega t = \frac{1}{2}(1 - \cos 2\omega t)$$

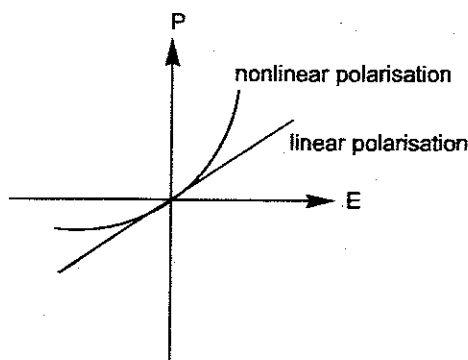


Fig. 1 Linear and nonlinear polarization versus electric field.

There is an important symmetry constraint for observing second-harmonic generation or other quadratic (in general any even order) NLO effects. The quadratic and other even-order effects are possible only in noncentrosymmetric systems. In a gaseous or liquid state where random fluctuations create a center of symmetry, one needs an alignment of molecules using an external field to break the center of inversion and observe second-order effects. However, in the case of third-order nonlinearities, there is no such symmetry constraint. Thus, in this article, we deal exclusively with second-order nonlinear optical properties of organic materials because of the important role of supramolecular chemistry in designing noncentrosymmetric systems.

## SECOND-ORDER NONLINEAR OPTICAL MATERIALS

Most of the materials developed initially for NLO applications were based on inorganic systems. Ferroelectric materials lacking a center of symmetry were prime candidates. With inorganic materials, the optical and acoustic phonons as well as the electronic polarization contribute to the NLO effects. The NLO effects in inorganics can be interpreted only at a bulk level; extension of the atomic or ionic polarizabilities to the bulk NLO properties is complicated. There is growing interest in developing  $\pi$ -conjugated organic molecules for NLO applications.

The molecular structures of some well-known systems are presented in Fig. 3. It was established that push-pull organic molecules have very high values of  $\beta_{ijk}$  (Eq. 2) and when they crystallize in a non-centrosymmetric space group, they possess large nonlinear susceptibility. The nonlinearity in these systems is dominated by electronic polarization effects. In the solid state, these organic compounds form molecular crystals in which the molecules interact through weak intermolecular forces and retain their individual identity to a high degree.

The quadratic NLO active molecules are mostly based on donor-acceptor substituted aromatics; benzene, stilbenes, diaryl acetylenes, diacetylenes, and biaryls are commonly used frameworks. In addition to the above materials, many more organic and organometallic compounds were examined by the powder SHG method, or their molecular hyperpolarizabilities were measured using EFISHG/HRS techniques, or both.<sup>[16-19]</sup>

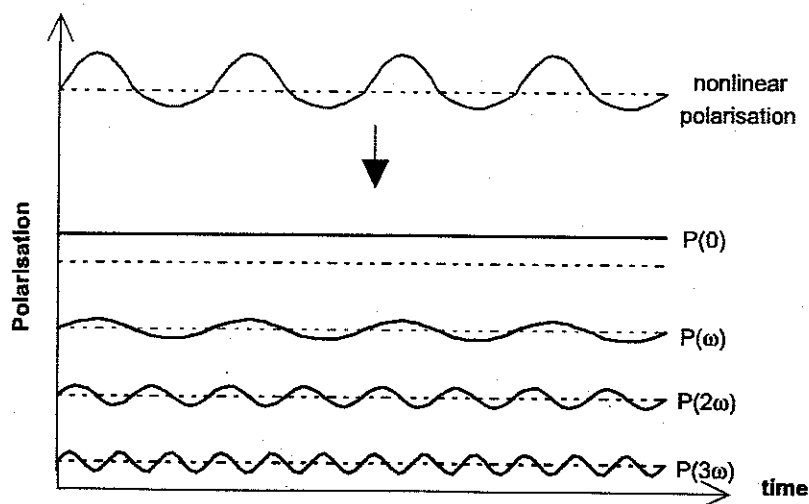


Fig. 2 The Fourier decomposition of nonlinear polarization and the components of  $P(x)$  at frequencies 0,  $\omega$ ,  $2\omega$ , and  $3\omega$ . (View this art in color at [www.dekker.com](http://www.dekker.com).)



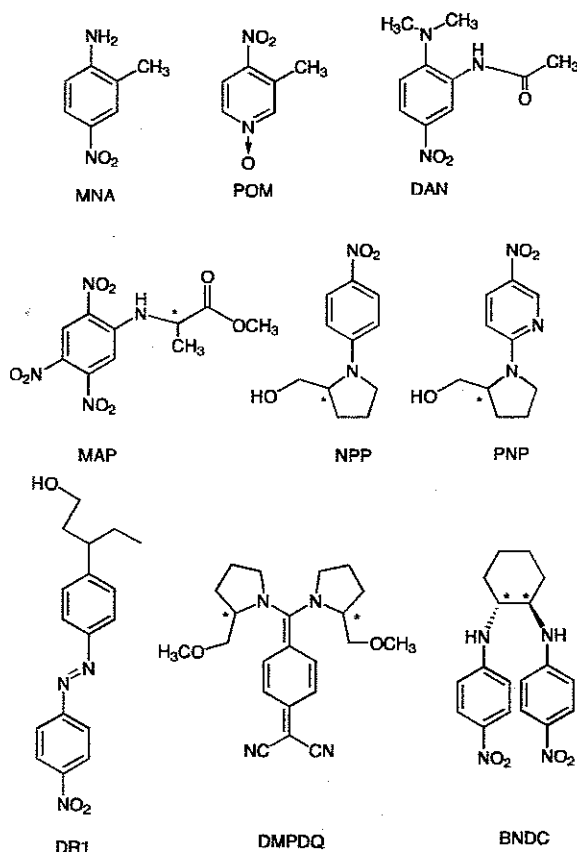


Fig. 3 Well-known organic NLO molecules.

### STRATEGIES TO OBTAIN NONCENTROSYMMETRIC STRUCTURES FOR QUADRATIC NLO APPLICATIONS

In the previous section, we already noted that a noncentrosymmetric structure is essential for a material to show second-order NLO properties. Amorphous and glassy solids are, in general, centrosymmetric. A majority of crystalline organic materials are also centrosymmetric. A variety of techniques were attempted to induce a noncentric lattice formation. Thin films can be prepared as noncentrosymmetric structures, using special techniques. Some of the popular strategies developed to induce noncentrosymmetry in bulk structures are as follows: inclusion of chirality in the molecule; utilization of crystal engineering techniques that exploit weak intermolecular forces; electric field poling of thin films or polymer films in which the molecules of interest are bound physically or chemically; preparing X, Z, or alternate-type Langmuir-Blodgett (LB) films; and layer-by-layer molecular self-assembly for generating intrinsically non-

centric super lattices. These methods are discussed in some detail below.

### Crystal Engineering

#### Inclusion of chirality

The utility of chirality for the fabrication of NLO organic materials was recognized very early in the case of amino acids and sugars.<sup>[1]</sup> Molecular chirality guarantees the crystallization of a pure enantiomer in one of the 21 noncentrosymmetric space groups. Achiral molecules generally crystallize in a centric lattice, though some important exceptions are known, e.g., urea (P4<sub>2</sub>m), benzil (P3<sub>2</sub>), *m*-nitroaniline, mNA (Pbc2<sub>1</sub>), MNA (Cc), POM (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>), and 3-acetamido-4-dimethylaminonitrobenzene, DAN (P2<sub>1</sub>). On the other hand, a pure enantiomer must crystallize in an enantiomorphous space group, and there are plenty of examples of such systems. Some well-known cases are MAP (P2<sub>1</sub>), NPP (P2<sub>1</sub>), and PNP (P2<sub>1</sub>) and TCNQ-based push-pull quinonoid molecule, DMPDQ (Fig. 4).<sup>[24]</sup> Though a mixture of equal quantities of a pair of enantiomers, i.e., a racemate, usually crystallizes in centrosymmetric space groups, some cases of crystallization in enantiomorphous space groups are also known. We note that the optical activity of a molecule only guarantees a noncentric lattice structure, but does not guarantee usefulness as a material for SHG. This is because the polarizable part of the molecules may still be aligned almost antiparallel, resulting in near cancellation of the NLO response of the molecules that are so aligned. It is important to have the NLO chromophores turned away from an antiparallel alignment to generate good SHG capability. In spite of this, the utilization of optical activity appears to be one of the most successful techniques for the generation of noncentric crystal structures, especially when used in conjunction with one of the following techniques. From Fig. 4, the effect of inclusion of

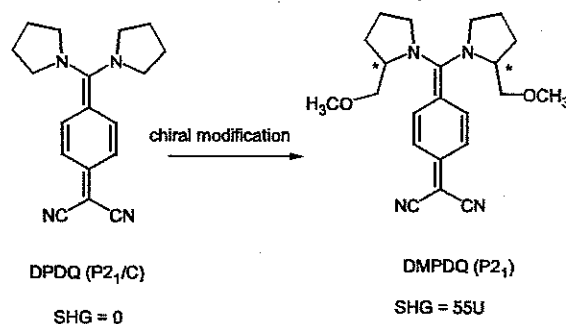


Fig. 4 Chirality-induced noncentrosymmetry and nonlinearity.



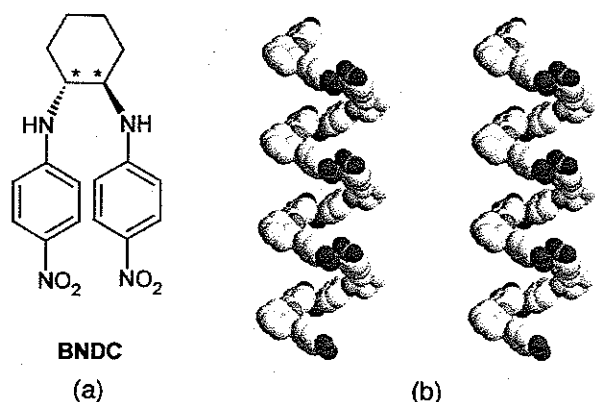


Fig. 5 (a) Molecular structure of BNDC and (b) helical superstructures of BNDC formed during crystallization. Reprinted with permission from Ref. [28]. Copyright (2001) Wiley-VCH. (View this art in color at [www.dekker.com](http://www.dekker.com).)

chirality in a molecule on its crystal space group and bulk NLO property is clearly seen.<sup>[20]</sup>

#### Intermolecular H-bonding

Hydrogen bonding is a well-known crystal engineering tool used to obtain desired crystal packing.<sup>[21]</sup> In the field of NLO, it was also used to get optimized noncentric structures in the organic crystals. The hydrogen bond bridges two atoms that have high electronegativities (such as O, N), and this can strongly influence the crystal structure and the spectroscopic properties of the molecules. Some examples of NLO systems where H-bonding has been crucial are, *o*-nitroaniline and its derivative, MAP, and urea. Urea is an extreme case of a hydrogen-bonded network.<sup>[1]</sup> The urea molecule that has eight atoms is involved in eight hydrogen bonds (four to each carbonyl and one each from each of the hydrogens). In urea, the hydrogen bonding played a crucial role in evolving a noncentric crystal structure.<sup>[10]</sup> Even though H-bonding affects the crystal structure in many significant ways, it is known to have a negligible effect on the molecular hyperpolarizabilities. Some theoretical investigations<sup>[11]</sup> do, however, indicate that in special

cases molecular  $\beta$ s are influenced mildly by H-bonding. The weak interactions between iodo and nitro groups that form supramolecular synthons were also exploited for designing materials for SHG.<sup>[22]</sup>

Recently, Radhakrishnan et al. reported the formation of a perfectly polar lattice in the crystal of (4-dimethylaminopyridyl) bis(acetylacetonato) zinc (II) (ZNDA).<sup>[23]</sup> This is one of the best examples of molecular assemblies that aligned noncentrosymmetrically in the lattice and is useful as a prototype for engineering polar supramolecular assemblies for NLO applications. In another article, they also reported<sup>[24]</sup> the formation of helical superstructures (Fig. 5b) from a simple crystallization of the  $C_2$ -symmetric and chiral *N,N'*-bis(4-nitrophenyl)-(1R-2R)-diaminocyclohexane (BNDC, Fig. 5a), which showed strong second-harmonic generation comparable to that of a well-known NLO compound, NPP. This study suggests that the control of supramolecular organization by molecular structure and symmetry can be a useful strategy in induction and enhancement of solid-state SHG in molecular materials.<sup>[25]</sup>

#### Poling of Doped Polymer Films

Polymer films with exceptionally large second-order nonlinearities can be produced by the corona poling (Fig. 6) process.<sup>[26]</sup> An efficient NLO chromophore molecule is either doped in a host polymer matrix or covalently linked as pendant groups on a polymer backbone. The polymer is then cast as a film, usually by spin-coating techniques. Subsequently, the film is subjected to a strong external dc electric field and heated to the glass transition temperatures of the polymer. At this point, the chromophores are aligned parallel by the field and locked into position when the film is cooled to room temperature with the external field on.

The poling thus leads to the alignment of doped molecules in the polymer films according to the Boltzmann distribution law. The oriented molecular dipoles produce a polarization,  $P = N\mu(\cos\theta)$ , where  $N$  is the number density of the molecules,  $\mu$ , the ground state dipole moment, and  $\theta$ , the angle between the dipole and the direction of the poling field. This method can

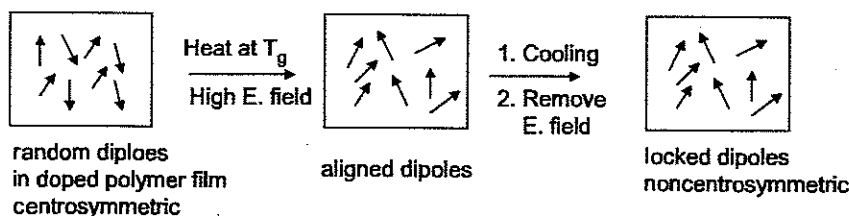
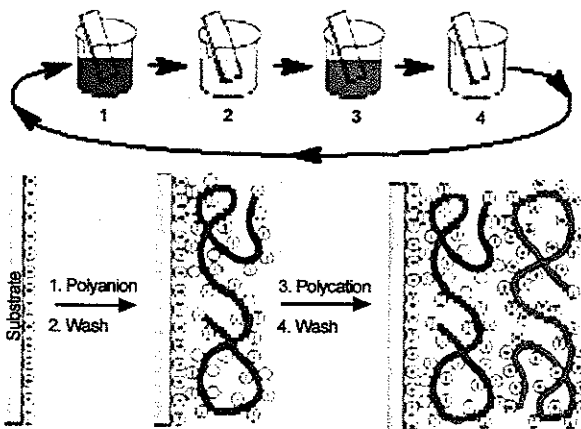


Fig. 6 Orientation of chromophoric dipoles under high electric field using corona poling in doped polymer films.





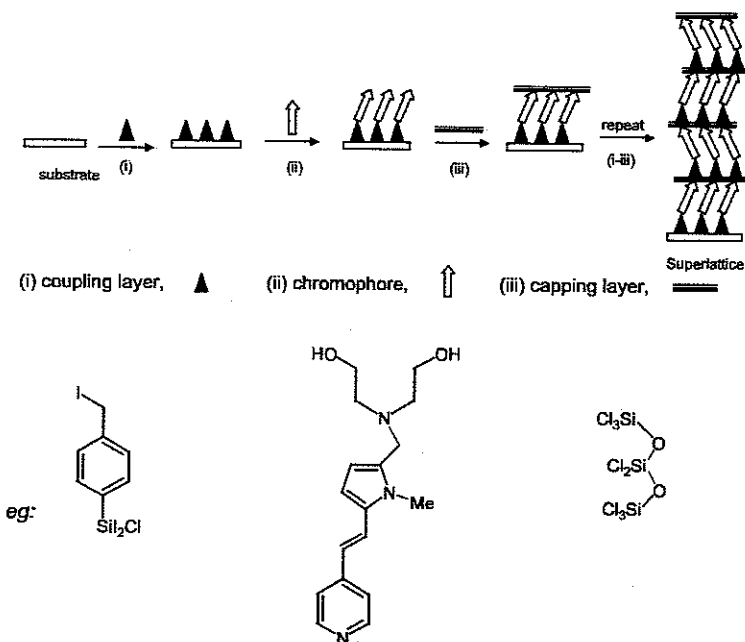
**Fig. 7** Procedure for electrostatic layer-by-layer assembly. Reprinted with permission from Oliveira et al. (Ref. [29]). (View this art in color at [www.dekker.com](http://www.dekker.com).)

also be used for functionalized and cross-linkable polymer matrices. The resulting polymeric material is of high optical quality and suitable for wave-guided electro-optic devices. The main problem associated with the poled polymer is the metastability of the system. After the external field is removed, the poled orientation

of the chromophores slowly gets randomized over a period of time, and hence, the noncentrosymmetry generated is lost. This destroys the quadratic NLO capability. Post-poling treatments such as cross-linking have to be undertaken to arrest the depoling process.

### Langmuir-Blodgett (LB) Films

Another approach to the construction of efficient thin-film-based SHG materials has been to incorporate NLO chromophores into acentric X- or Z-type LB films.<sup>[1]</sup> This approach offers far greater net chromophore alignment than is possible in a poling field (where the net alignment is statistical). LB films are built up from amphiphilic molecules, i.e., molecules having a hydrophilic part and a hydrophobic part. The preparation of the LB film consists of the following steps. The amphiphilic molecule is first dissolved in a solvent immiscible with water, and the solution is spread onto the clean water surface in a Langmuir trough. The solvent is left to evaporate, leaving the molecules spread on the water surface. The Langmuir trough is equipped with a mobile barrier to compress the film laterally. The film is gradually compressed to a surface pressure just below its collapse pressure. Because of their long aliphatic chains, the molecules cannot



**Fig. 8** Assembly of chromophoric super lattices by an iterative sequence of (i) covalent chemisorption of (*p*-iodomethyl)-phenyl-dichlorosilane onto hydrophobic substrates to form a "coupling" layer, (ii) spin-coating of a methanol solution of chromophore precursor followed by vacuum oven treatment, and (iii) reaction of the quaternized-chromophore-based monolayer with octachlorosiloxane. Reprinted with permission from Ref. [31b]. Copyright (2003) American Chemical Society. (View this art in color at [www.dekker.com](http://www.dekker.com).)



dissolve in water, and due to their hydrophilic group, they cannot leave the water surface. Hence, they form a compact, monomolecular, and in many instances, stable film at the water-air interface. When a hydrophilic substrate previously immersed is slowly raised through the monolayer, deposition takes place with the hydrophilic group attached to the substrate and the hydrophobic part sticking out. Subsequent dipping creates a head-to-head or tail-to-tail arrangement of the amphiphiles deposited as multilayers on the substrate. By the above method, one prepares an LB film that is basically centrosymmetric (called Y-type). Such films are not suitable for optical second-harmonic generation. The X- and Z-type films with a head-to-tail arrangement and, hence, a noncentric bulk arrangement can be prepared with relatively low-polarity hydrophilic groups or with special functionalization of the hydrophobic chain ends.

Another approach is to prepare alternate layered films of the type A-B-A-B-A-B, wherein one of the molecules A or B is the active NLO chromophore and the other is just a binding spacer unit.

### Layer-by-Layer (LBL) Molecular Assembly

Orientation of nonlinear optical active dyes in electrostatically self-assembled polymer films containing cyclodextrins was studied.<sup>[27]</sup> The concept of molecular recognition of organic chromophores by coordinating polymers was another novel approach in the construction of nonlinear optical supramolecular assemblies.<sup>[28]</sup>

Electrostatic layer-by-layer (LBL) self-assembly techniques based on oppositely charged polyelectrolytes can be useful to create stable noncentrosymmetric order in thin films. Using this interesting technique, thermodynamically stable noncentrosymmetric multilayer films can be prepared without any need for poling. Tripathy et al. reported the fabrication stable multilayer films of epoxy-based side chain azo polymers for second-order nonlinear optics.<sup>[29]</sup> The second-order NLO coefficients of the five-bilayer LBL films of these polymers were found to be comparable to those of spin-coated poled films. A schematic view of the procedure to fabricate polyelectrolyte-based LBL films is shown in Fig. 7.

Since 1990, self-assembly techniques involving covalent linkages and layer-by-layer fabrication were reported to yield robust noncentric super lattices highly suited for applications such as SHG and electro-optic effects.<sup>[30-33]</sup> Spontaneous and sequential adsorption of appropriately derivatized adsorbates onto substrates in a self-limiting fashion can yield thin films with uniform polar orders in individual layers. This represents an attractive approach to the construction of intrinsically acentric chromophoric super lattices. Li et al.<sup>[30]</sup> reported synthetic routes to the

first SHG-active multilayer structures using an attractive covalent siloxane self-assembly approach, highly regular and highly nonlinear [ $\chi^{(2)} \sim 200$  pm/v at  $\omega = 1064$  nm] self-assembled stilbazolium multilayers were constructed in a regular, layer-by-layer fashion. Recently, the synthesis of super lattices of pyrrole-based diethanolamino methyl functionalized derivatives was reported and is described in Fig. 8.<sup>[31]</sup> The key feature to self-assembled multilayers is that the microstructural acentricity is maintained, and thus, they show the quadratic dependence of the SHG response on the number of assembled layers. These multilayers have good structural reproducibility and are suitable for efficient NLO properties as was reported for the second-order nonlinear optical susceptibility [ $\chi^{(2)} \sim 150$  pm/v at  $\omega = 1064$  nm] for the chromophore in Fig. 8.

### CONCLUSION

In this article, we discussed the basic concept of nonlinearity and fabrication of noncentrosymmetric structures using well-known strategies like crystal engineering, corona poling, LB films, and molecular assembly of acentric structures. The role of supramolecular chemistry in developing efficient NLO materials is clearly delineated. Though physical methods like poling and LB techniques are successful strategies for creating noncentrosymmetric materials for NLO, the design of molecular chromophores with specific groups and functionalities for creating noncentrosymmetric materials through crystal engineering is still a fascinating subject to chemists and material scientists. Molecular assembly via synthesis is also a well-accepted strategy for fabricating covalent, robust, noncentrosymmetric structures for electro-optics and many other controlled structures for applications like light-emitting diodes, sensors and photovoltaics, etc. In the forthcoming years, the approaches of creating layer-by-layer molecular assemblies synthetically or by ionic adsorption may lead to other approaches and provide new methodologies for materials chemistry.

### ACKNOWLEDGMENT

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### ARTICLES OF FURTHER INTEREST

*Concepts in Crystal Engineering*, p. 319

*Crystal Engineering with Hydrogen Bonds*, p. 357



*Hydrogen Bonding*, p. 658  
*Hydrophobic Effects*, p. 673  
*Layered Supramolecular Solids and Their Intercalates*,  
 p. 791  
*Molecular Switches*, p. 917  
*Molecular Wires*, p. 925  
*Space Groups and Crystal Packing Modes*, p. 1337  
*Strict Self-Assembly and Self-Assembly with Covalent  
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*van der Waals Forces*, p. 1550  
*X-Ray Crystallography*, p. 1586

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